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Sulfonated poly(ether ether sulfones) Characterization and study of dielectrical properties by impedance spectroscopy

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Abstract

In this work, three samples of sulfonated polysulfones of different sulfonation degree have been characterized, and the electrical properties of dense membranes based on them have been evaluated. The polymers were characterized spectroscopically, and by their inherent viscosity, and water absorption. Electrical characterization of membranes was carried out on dense membranes in contact with NaCl solutions, by impedance spectroscopy (IS) measurements using equivalent circuits as models. The results showed how the sulfonation clearly affected the membrane electrical characteristics, strongly reducing the membrane resistance, and also changing the type of circuit associated to the membrane, which could be related to the increase of electrolyte taken by the membrane when the sulfonation degree increased. Concentration dependence of the electrical parameters was also studied.

Keywords: Polysulfone; Sulfonated; NMR; Water up-take; Impedance spectroscopy

1. Introduction

Polysulfones are a class of engineering thermoplastics that have achieved special importance in the manufacturing of asymmetric and composite membranes. As a matter of fact, most of the commercial thin film composite (TFC) membranes used at present in desalination of sea water and brackish water, consist of an active selective thin layer of less than 1 μm of a hydrophilic polymer supported by a microporous thick layer (50–100 μm) of polysulfone [1–3]. Polysulfones are not hydrophilic, actually they are quite hydrophobic, so that it would be desirable to raise the water affinity of polysulfones in order to improve their properties as supporting layers for water purification membranes.

Sulfonic groups have demonstrated to be very suitable for these purposes [4,5]. The ionic nature of these groups greatly enhances the transport of water through membranes, and the improvement of hydrophilicity helps for the membranes to become more fouling-resistant. Furthermore, sulfonated polymers are a kind of ionomers known since many

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years as strong ion exchange materials, particularly cation exchange membranes, suitable, for instance, in electrolysis cells and electrodialysis, and as resins for the treatment of hard waters [4,6,7]. Sulfonated polymers have got recently importance also as materials for fuel cell membranes, where a strong demand has arisen for polymer electrolytes [8,9].

Sulfonated polysulfones offer an attractive alternative regards the applications mentioned earlier. On preparing modified polymers there are always two main approaches to adopt, either synthesizing polymers from new monomers, especially designed for the modification, or treating the parent polymer with suitable reagents. In the case of polysulfones, the treatment of the polymers is the preferred route as the polymers are commercially available and they can be treated in solution, or even in the molten state. Nevertheless, sulfonation of conventional polysulfones based on bisphenol A is far from being an easy process, and some specific methods have had to be outlined to effectively incorporate sulfonic groups on the aromatic rings of polisulfones [10–13]. Furthermore, poly(ether sulfone)s are fully aromatic polymers that do not offer favourable structural conditions to be sulfonated as they consist of para-oriented benzene rings that are always linked to a sulfonyl group, an electron acceptor group that effectively deactivates the ring for electrophilic attack.

Sulfone copolymers like poly(ether ether sulfone)s (PEES) do actually offer a favourable alternative to obtain sulfonated materials. They contain a number of phenyl ether units that can readily react with conventional sulfonation agents, to render materials with a wide range of sulfonation degree [14,15]. Because of the potential technical interest of these ionic materials, it seemed interesting to study the electrochemical behaviour of a series of them. Thus, the purpose of this work was to evaluate the electrical properties of dense membranes based on sulfonated poly(ether ether sulfone)s with different sulfonation degree.

Electrical characterization of membranes was carried out by electrochemical impedance spectroscopy (EIS). The EIS is a non-destructive technique which is being used as a successful tool to obtain the electrical properties of heterogeneous systems such as membrane/electrolyte systems, since it allows to determine separately the electrical contributions of both membrane and electrolyte solution [16–18]. Using equivalent circuits as models, membrane electrical parameters (resistance, capacitance and Warburg impedance) were evaluated [19,20] and discussed, trying to establish properties–structure relationships.

2. Experimental

2.1. Polymers

Experimental powdered sulfonated poly(ether ether sulfone)s (SPEESs) were supplied by Imperial Chemical Industries, UK. They were characterized by their inherent viscosity (determined on 0.5% polymer solutions in *N*-methylpyrrolidinone), and NMR spectra (^{1}H NMR spectra made in deuterated dimethylsulfoxide using a Varian Gemini spectrometer, operating at 200 MHz). Water sorption was measured on approximately 1 g samples of each polymer, after having been dried in a vacuum oven at 100°C for 24 h, over phosphorus pentoxide. The samples were stored in a closed box at 65% humidity and 25°C, and they were weighed at fixed time intervals until equilibrium was achieved.

2.2. Membranes

All the membranes were cast from *N*,*N*-dimethylacetamide (DMA) solutions. Generally, 15% (w/w) solutions were used, that were cast on levelled glass plates, and spread with normalized bars to leave a thickness of approximately 300 μm. The solvent was removed in several steps, first most of the solvent was evaporated in an oven at 80°C for 24 h, then the film was stripped off in a water bath and dried in a vacuum oven at 110°C for 6 h, and finally at 120°C and 0.1 mm Hg for 3 h. Creasable, strong films could be attained in every case. The thickness of the films were determined by a digital micrometer (Digimatrix Marck II).

The membranes were treated with a solution 0.1 M of HCl or NaCl for 8 h, to remove any cation other than H^+ or Na^+ (membranes in H^+ form or Na^+ form, respectively), then they were washed with distilled water until the rinse water was neutral.

2.3. Electrochemical impedance measurements

Impedance measurements were carried out in a test cell similar to that described elsewhere [21]. It

basically consists of two half-cells separated by the membrane, which was fixed between two rubber rings, with platinum electrodes connected to an impedance analyzer (Solartron 1260) from which data can be sent to a computer for further treatment and storage. Due to the great difference in the electrical resistance showed by the membranes, cells with different sample area were used but, in all cases, the distance between the electrodes was 2.5 cm, and the electrode area was always larger than the membrane area exposed to flow in order to ensure the homogeneity of the electric field. The experimental data were corrected by the software, taking into account the influence of connecting cables and other parasite capacitances. Measurements were made with 100 different frequencies in the range $10–1\times10^6$ Hz at a maximum voltage of 0.01 V and different NaCl concentrations ($10^{-3}\leq C\leq 5\times10^{-2}$ M).

Measurements were carried out at room temperature and standard pH (t=25°C, pH=6.2±0.3), with both half-cells filled with solutions of identical concentration. Before using, the membranes were immersed for at least 8 h in a solution of the appropriate salt concentration. In order to avoid changes in the pH of the solutions when the sulfonated samples were used, the cell was filled with fresh solutions just before measuring.

3. Theory

Impedance Spectroscopy (IS) is a relatively new technique for characterizing materials and interfaces, that has emerged with the development of instruments able to measure impedance as a function of frequency in the 10^{-6}–10^9 Hz range [22]. One of the most important features of IS comes by the development of direct correlations between the response of a real system and an idealized model circuit composed of discrete electrical components. Phenomenologically, a resistance (R) is taken to represent the dissipative component of the dielectric response, while a capacitance (C) describes the storage component of the dielectric material. If a R–C parallel circuit as that shown in Fig. 1a is considered, it represents an adequate model of the dielectric polarization in the frequency range dominated by the migration of free charges. The overall impedance of this circuit is given by the sum of capacitance and resistance contributions

$$\frac{1}{Z^*} = \frac{1}{R} + j\omega C \tag{1}$$

The complex impedance Z^* can be separated into real and imaginary component by algebra rules

$$Z_{\text{real}} = \frac{R}{1+(\omega RC)^2}, \qquad Z_{\text{img}} = \frac{-\omega R^2 C}{1+(\omega RC)^2} \tag{2}$$

Analysis of the impedance data is often carried out by a complex plane method, which involves plotting the impedance imaginary part against the real part ($-Z_{\text{img}}$ versus Z_{real}). Thus, different equivalent circuits can be obtained from the plots

- The equation for a parallel R–C circuit gives rise to a semi-circle in the Z^* plane, as is also shown in Fig. 1a, with intercepts on the Z_{real} axis at

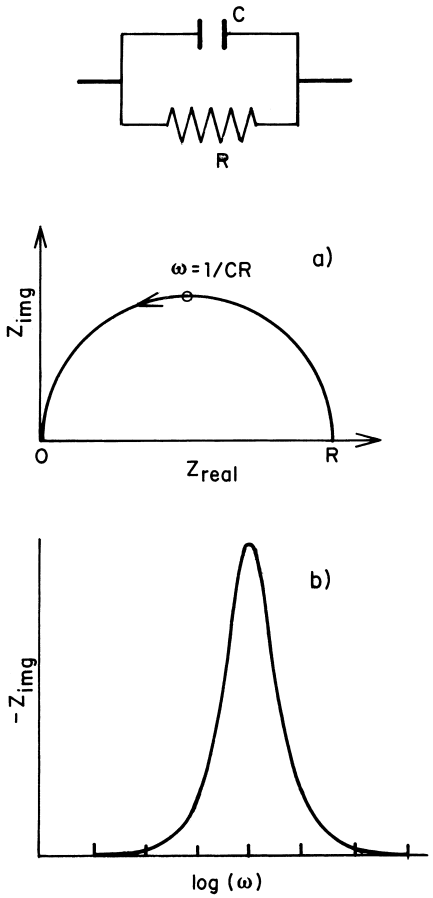

Fig. 1. Equivalent circuit of an electrochemical cell; R: resistor, C: capacitor. Representation in the Z_{img} plane: (a) Nyquist plot and (b) Bode plot ($-Z_{\text{img}}$ vs. log f).

R_∞ ($\omega \Rightarrow \infty$) and R_0 ($\omega \Rightarrow 0$), being (R_0–R_∞) the resistance of the system. The maximum of the semi-circle equals 0.5 (R_0–R_∞) and occurs at such a frequency that $\omega RC=1$, RC being the relaxation time [22].

- Complex systems may present different relaxation times, and the resulting plot is a depressed semi-circle as that shown in Fig. 1b. In these cases a non-ideal capacitor, which is called a constant phase element (CPE), can be considered, with impedance expressed by

$$Q(\omega) = Y_0(j\omega)^{-n} \tag{3}$$

where the admittance Y_0 ($\Omega\,s^{-n}$) and n are experimental parameters ($0 \leq n \leq 1$) [22]. Two special cases depending on the n parameter can be considered: if $n=1$, it corresponds to an ideal capacitor, if $n=0.5$, the element circuit is called a Warburg impedance, W, which is associated with a diffusion process according to Fick's first law.

In the case of complex systems, an equivalent capacitance (Ceq) can be determined by the relationship [23]

$$C^{eq} = \frac{(RY_0)^{1/n}}{R} \tag{4}$$

These expressions indicate that electrical characteristic parameters for homogeneous or heterogeneous systems can be obtained by EIS measurements.

4. Results and discussion

4.1. Polymers characterization

In order to get reliable correlations between chemical composition and electrical properties, a careful characterization of the samples was done, using NMR spectroscopy, viscosimetry and water up-take determinations.

The SPEESs subject of this study were experimental polymers, that had been prepared from defined mixtures of monomers, namely hydroquinone (1,4-dihydroxybenzene), 4,4′-dihydroxydiphenylsulfone and 4,4′-dichlorodiphenylsulfone, and then sulfonated under the conditions previously reported [14]. Only the hydroquinone units can be substituted on treating PEESs with sulfonating agents, and only one sulfonic group can be incorporated per hydroquinone moiety. If the sulfonation reaction proceeded up to 100% conversion, the chemical structure of the SPEESs would be as depicted in Fig. 2.

A reliable method to confirm the composition of the polymers is to analyze them by ^{1}H NMR spectroscopy. That was the method used here to investigate the chemical structure of three samples of SPEESs, with a theoretical sulfonation degree of 5, 10 and 20%, respectively ($x=0.05$, 0.1 and 0.2). A non-sulfonated PEES with $x=0.4$ and $y=0.6$ was used as standard to help for the assignation of the NMR spectra signals.

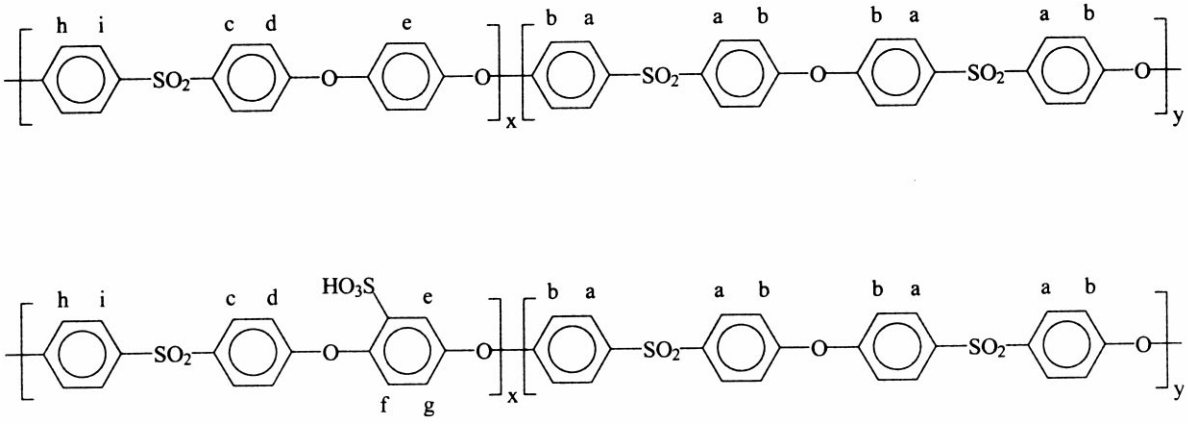

Fig. 2. Repeating unit of PEES and SPEES.

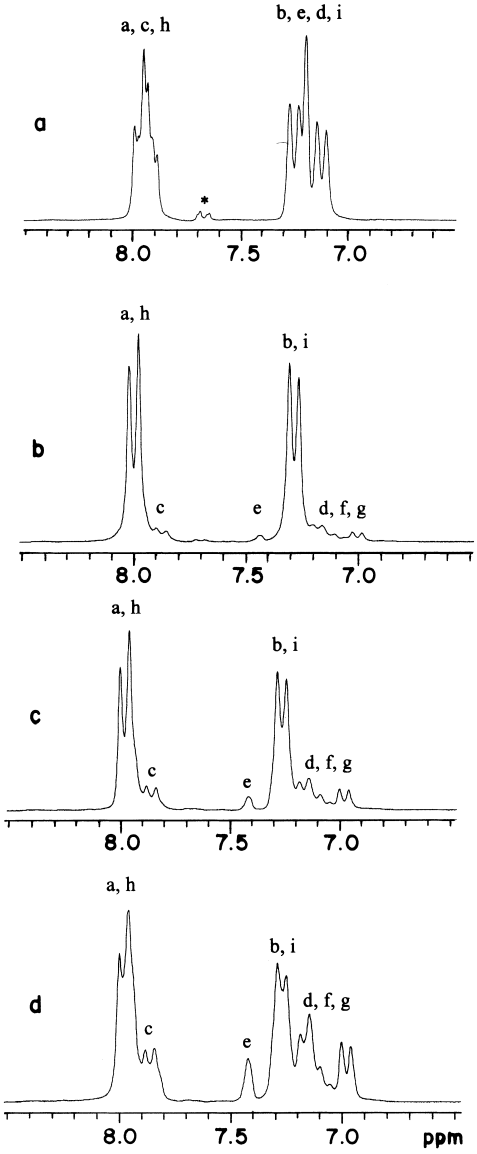

Fig. 3. ^{1}H NMR spectra of non-sulfonated and sulfonated poly(ether ether sulfone)s: (a) SG0; (b) SG5; (c) SG10 and (d) SG20.

Fig. 3 reproduces the ^{1}H NMR spectrum of the reference PEES along with the spectra of the three sulfonated PEES. All the signals of spectrum (a) could be assigned, and the integration of the peak areas unequivocally confirmed the composition (40/60 of the polymer). The incorporation of SO_3H groups on the hydroquinone units greatly affected the spectra, as can be seen in Fig. 3b–d. For analytical purposes, the peak at 7.44 ppm is particularly interesting as it appeared only in the spectra of sulfonated species. This signal corresponds to the hydrogen orto to the sulfonic group, so that it could be taken as a reference to define the range of chemical shift that separates the signals of protons neighbor to ether linkages (high field, below 7.6 ppm) and the protons neighbor to sulfonyl groups (low field, over 7.6 ppm). A simple equation had to be solved to calculate x and y for each polymer once the peak areas could be experimentally measured

$$x + y = 1 \tag{5}$$

$$\frac{A_{\mathrm{lf}}}{A_{\mathrm{hf}}} = \frac{2y}{(2y + 3x)} \tag{6}$$

where A_{lf} is the area under the signals at low field (over 7.6 ppm) and A_{hf} is the area under the signals at high field (below 7.6 ppm).

By applying Eqs. (5) and (6), the samples were calculated to contain 4.5, 9.3 and 19.4% of sulfonated units, respectively. Theoretically, they should be 5, 10 and 20%, according to the feeding of monomers and considering full conversion for the sulfonation process. Thus, the determination of the composition by NMR confirmed a good agreement between the experimental and the expected sulfonation degree of the SPEESs, and membranes made from these polymers will thereafter be called SG5, SG10 and SG20, respectively, while the non-sulfonated membrane is named SG0.

Viscosity measurements revealed that the sulfonation reaction did virtually not modify the molecular weight of the polymers. Inherent viscosities values in the range 0.55–0.74 dl/g were found for the SPEESs, that compare well with the viscosity of the reference non sulfonated sample, 0.66 dl/g, and with commercial engineering thermoplastics based on poly(ether sulfone)s. For instance, Victrex® PES for general purposes, measured in the same conditions, showed an inherent viscosity of 0.61 dl/g.

The determination of water up-take is important for polymers that are expected to be used in contact with aqueous solutions. Therefore, the water sorption was measured for all the samples, and depicted as the gain in weight when exposed to an atmosphere of controlled humidity. Isothermal sorption curves, shown in Fig. 4, were a clear dependence of the water up-take on

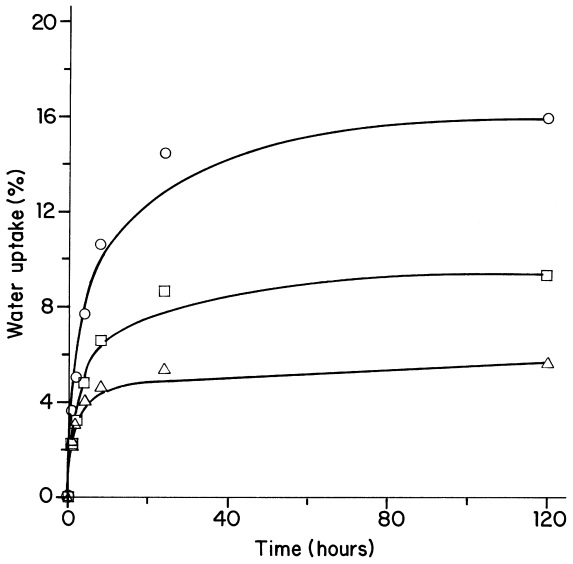

Fig. 4. Water uptake isotherms of SPEES: SG5 (△); SG10 (□) and SG20 (○).

the sulfonation degree can be observed. With a maximum water sorption of ca. 16%, for SG-20, SPEESs appear as hydrophilic materials when compared with unmodified polysulfones and polyethersulfones, that show values of only 1.0–2.0% water sorption in the equilibrium [24].

4.2. Electrical characterization

Fig. 5 shows the impedance plots ($-Z_{img}$ versus Z_{real}) for the different membranes, at a given NaCl concentration, as well as the equivalent circuits associated to each membrane/electrolyte system. As can be seen from this picture, two different dielectric relaxations were obtained with SG0, SG5 and SG10 samples, one for the membrane and other for the electrolyte solution, but only a dielectric relaxation was obtained with the SG20 membrane, and it was a semicircle, which indicates only a relaxation time characteristic of a Debye behavior for the membrane/electrolyte solution system.

Fig. 6 shows the Bode plot ($-Z_{img}$ versus f) for SG5 and SG10 membranes, which allows the assignation of the frequency range for the electrical contribution of both membrane and electrolyte solution. A membrane contribution in the range $10 \leq f\,(\mathrm{Hz}) \leq 6\times10^4$ was observed, while the electrolyte contribution appeared at a frequency higher than 6×10^4 Hz. Similar curves were obtained with the different membranes and concentrations studied, so that only the membrane contribution will be considered in the following discussion.

The experimental values were fitted to the different circuits, which allowed to obtain qualitative information about the relationship between the transport behavior and the structural characteristics

1. For SG0 and SG5 the circuit corresponded to a parallel association of a resistance and a CPE element ($R_m Q_m$).
2. The circuit for the SG10 membrane was a parallel association of a resistance and a Warburg impedance ($R_m W_m$).
3. The electrical contribution of the SG20 membrane could not be separated from that corresponding to the electrolyte solution, and the circuit for the whole system consisted of a parallel association of a resistance and a capacitor (RC), as only a relaxation time for the whole system was found. This kind of behaviour had been previously reported for highly porous membranes completely embedded by the electrolyte solution [16,25–26].

Differences could be observed in the electrical resistance of the membranes depending on its ionic form (H^+ form or Na^+ form) as is illustrated in Fig. 7, where a comparison between the impedance plots for the SG5 sample in both ionic forms is shown. Slightly lower resistance values were obtained for the samples in Na^+ form, what seemed consistent with the higher dissociation constant of SO_3^- Na^+ in respect to SO_3^- H^+. Furthermore, an effect of protons conduction by Grotthuss translocation [27], seemed to be negligible compared to the ionic current provided by the solvated cations in the matrix of these dense SPEESs. On the other hand, no difference was found either in the type of circuit for each membrane or in the values of the other circuit parameters depending on its ionic form.

The experimental data for each membrane and each NaCl concentration, were fitted to the assigned equivalent circuit by means of a non-linear program [28], what allowed the calculation of the characteristic membrane electrical parameters (R_m, W or C), with relative errors lower than 8% in all cases. For the SG20 membrane, the electrical resistance was determined by subtraction of the electrolyte solution resistance values (R_e) from those obtained with

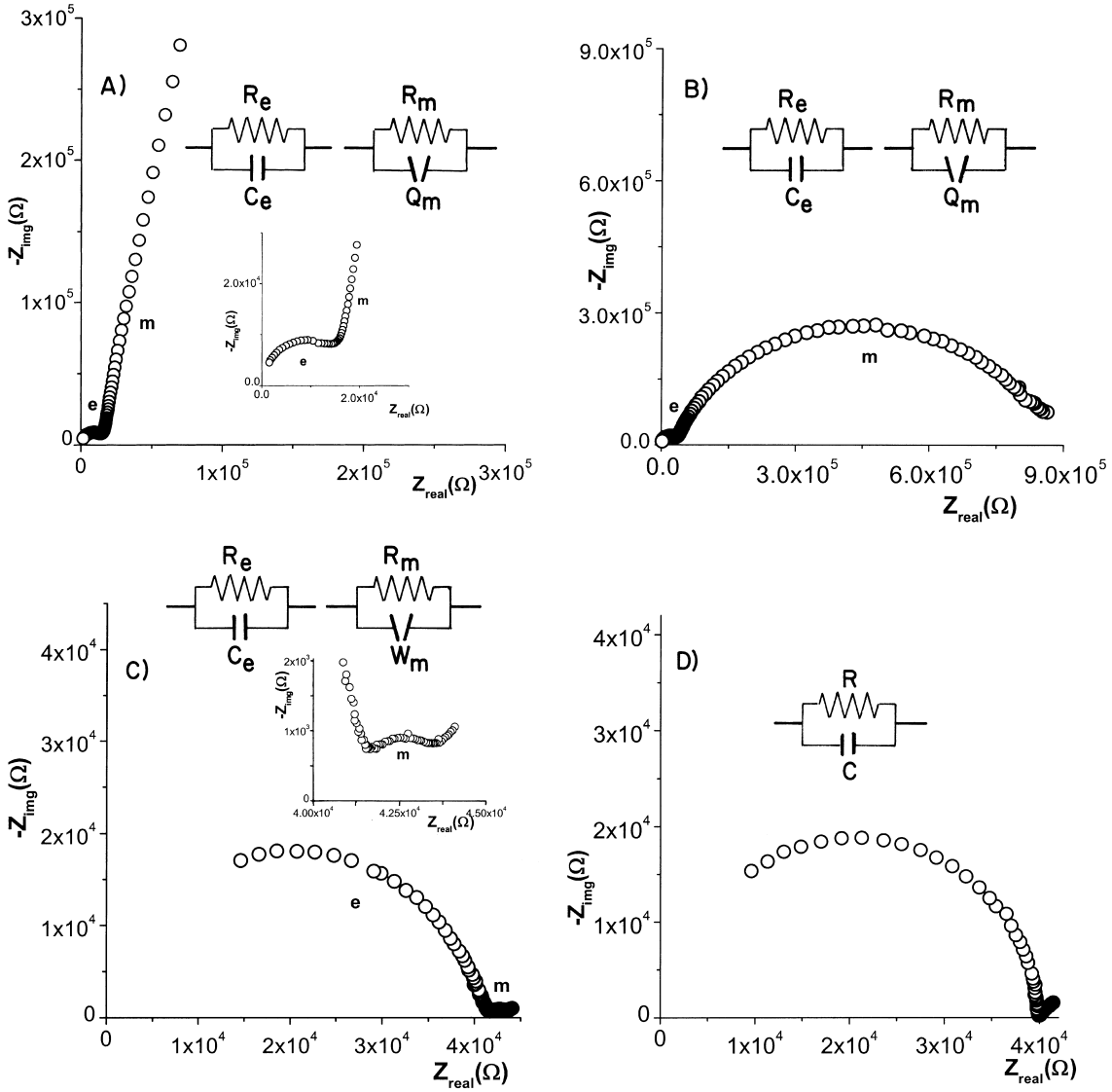

Fig. 5. Impedance plot for the different membranes (C=2.10^{-3} M): (A) SG0; (B) SG5; (C) SG10 and (D) SG20.

the membrane/electrolyte system (R_{sm}), that means $R_m = R_{sm} - R_e$. Due to the different thickness of the samples studied, membrane resistivities were calculated by the relation $r_m = (S/d)R_m$, where S and d are the area and the thickness of the membrane, respectively.

Plots of membrane resistivity versus salt concentration have been drawn in Fig. 8 for the different membranes in H^+ form and Na^+ form. As can be seen, results showed an important dependence of r_m on both sulfonation degree and salt concentration. Thus, an increase in the sulfonation degree strongly reduced the membrane resistance (or resistivity), but it also affected the value of the parameter n in Eq. (3). For the whole range of concentration and both ionic forms, the following average values of n were determined: $\langle n_{GS0} \rangle = (0.900 \pm 0.009)$, $\langle n_{GS5} \rangle = (0.76 \pm 0.03)$ and $n_{GS10} = 0.5$ (which is the theoretical value for a Warburg impedance). On the other side, significant differences were not appreciated in the equivalent

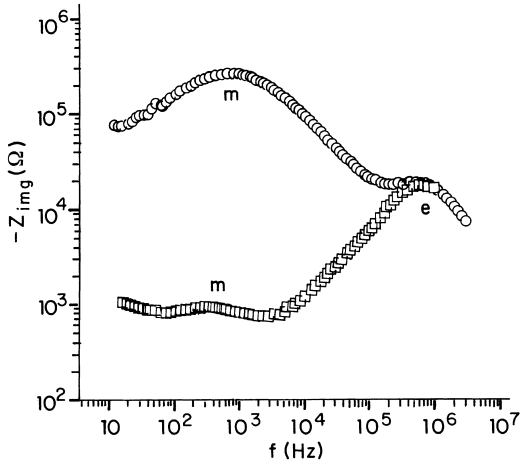

Fig. 6. Bode plot for : SG5 (○) and SG10 (□), at C=5.10^{-3} M.

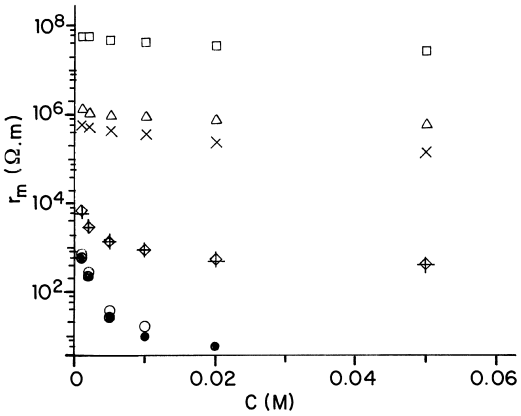

Fig. 8. Membrane resistivity, r_m vs. NaCl concentration for: SG0 (□); SG5: H^+ form (△), Na^+ form (×); SG10: H^+ form (◇), Na^+ form (+); and SG20: H^+ form (○), Na^+ form (●).

capacitance C^{eq}, determined by Eq. (4), for SGO and SG5 as a function of the salt concentration and ionic form. The values obtained were: $\langle C^{eq}{}_{GS0}\rangle$=(2.27±0.12)×10^{-10} F, $\langle C^{eq}{}_{GS5}\rangle$=(3.3±0.4)×10^{-10} F, and from these values, and assuming that the membranes behaved as plane capacitors, the following dielectric constants were obtained: $\langle\varepsilon_{SG0}\rangle$=(13±3) and $\langle\varepsilon_{SG5}\rangle$=(37±5). A similar increase of the Warburg impedance was obtained for the SG10 membrane with both ionic forms when the salt concentration increased.

The electrical conductivity of a synthetic membrane under the condition of equal electrolyte concentration

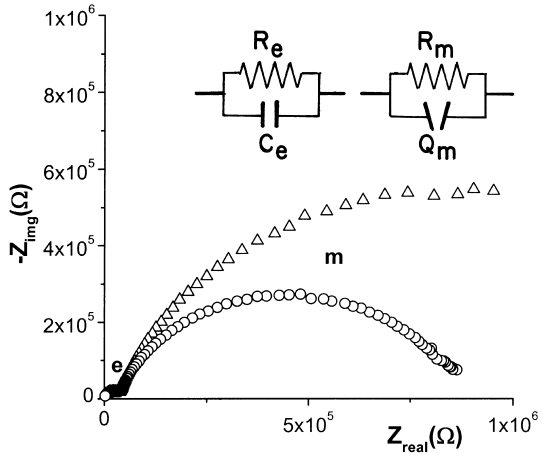

Fig. 7. Impedance plots for both ionic forms of the SG5 membrane: H^+ form (△) and Na^+ form (○).

on both sides of the membrane can be expressed by [29]

$$L_e = \left(\frac{F^2}{dRT}\right)\sum_i (z_i^2 D_i C_i) + L_p (X_f F)^2 \qquad (7)$$

where D_i, C_i and z_i are the diffusion coefficient, the concentration and the valency of the ion i, respectively, L_p is the membrane hydrodynamic permeability and X_f is the concentration of fixed charge in the membrane, R and F are the gases and Faraday constants and T is the temperature of the system. Eq. (7) shows that the membrane conductivity is composed of two terms, a diffusive component and a convective one, however, for dense membranes with small fixed charge the convective term can be neglected, and the following expression for the membrane resistivity can be considered:

$$r_m = \frac{RT}{F^2}\left(\sum_i z_i^2 D_i C_i\right) \qquad (8)$$

Fig. 9 shows a comparison between experimental resistivities and those calculated by Eq. (8). Resistivities could be calculated for SG0 and SG20 by using the values indicated in the literature for the diffusion coefficients of ions for dense membranes and solutions, respectively [29–31], and assuming a salt partition coefficient of 0.5. As can be seen in Fig. 9, quite good agreement between theoretical and experimental values was achieved, taking into account that factors

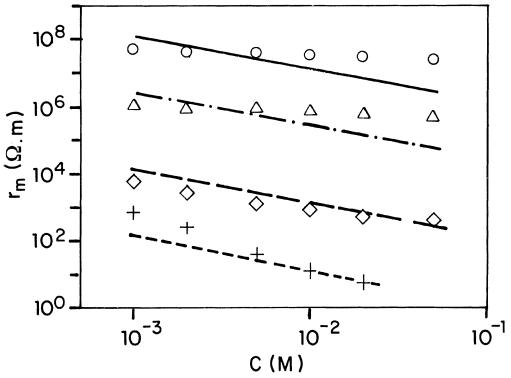

Fig. 9. Comparison of experimental membrane resistivity values with those calculated by Eq. (8): SG0 (○); SG5 (△); SG10 (◇) and SG20 (+). Calculated curves: SG0 (—); SG5 (–·); SG10 (–) and (-) SG20.

which could affect diffusion coefficients (i.e. concentration dependence) have not been considered. These results confirmed the previous assumptions on the effect of sulfonation on transport/structural membrane parameters.

5. Conclusions

These results show how the sulfonation clearly affects the properties of PEESs, particularly their spectroscopic characteristics, and water uptake, what, on turn, permits the characterization and quantitative determination of the sulfonation degree.

Furthermore, sulfonation greatly affects the electrical features of PEES membranes. While non sulfonated PEESs behave as genuine dielectric materials, impermeable to ions, and work as capacitors within a RC circuit, sulfonation strongly reduces the membrane resistance and, depending on the sulfonation degree, also changes the type of circuit associated to the membrane, which is related to the increase of electrolyte taken by the membrane when the sulfonation degree increases, and that is true for different electrolytes and concentrations [32].

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